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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to the resin composition which consists of a polymer with aliphatic ester structures, and polyolefine, and its mold goods.

[0002]

[Description of the Prior Art]Development of the polymers raw material which collapses in natural environment comes to be demanded to the environmental problem in a terrestrial scale in recent years, It has a hope as environmental suitability material or high-performance material new type with a great plastic which will collapse by the time it is decomposed by the microorganism and does not stop a prototype in particular in it.

[0003]It is known well that a polymer with aliphatic ester structures has biodegradability conventionally, The Polly 3-hydroxybutyric acid ester (PHB) produced by a microorganism, The polylactic acid (PLLA) etc. which used as the raw material L lactic acid produced by polybutylene succinate (PBS) and fermentation which use as the main ingredients polycaprolactone (PCL), succinic acid, and butanediol which are synthetic macromolecule are typical. This invention persons were excellent in the mobility and the moldability which have the high thermal stability of a statement in JP,7-53693,A and JP,7-53695,A, and developed biodegradable polyester carbonate which has sufficient mechanical strength, and a manufacturing method for the same.

[0004]The polymer with aliphatic ester structures is good polymer of the moldability and biodegradability which generally has the physical properties of polyethylene resemblance, when polylactic acid is removed. However, moisture permeability was high and, in the field as which the low moisture permeability of a film, a bottle, etc. is required, the improvement was desired without sufficient capability. With the film whose catabolic rate by a microorganism is early especially thin, decomposition may be too early and the relaxation is called for. Since it is a comparatively expensive material, the low-pricing is desired.

[0005]On the other hand, it is general purpose grade polymer which has long history, and polyolefine is derived mainly from a petroleum raw material, is excellent in physical properties, and cheap. However, in natural environment, it does not decompose but is

considered a high material of the environmental impact. Combustion heat and the danger of damaging an incinerator when it burns highly are pointed out. Therefore, it collapsed in environment and improvement which stops combustion heat was desired. Oxygen permeability is high and the necessity for the improvement is pointed out in packaging applications. As a trial which gives biodegradability to polyolefine and stops combustion heat, although examined by the blend with starch etc. for many years, there are many portions which remain without decomposition by a microorganism not being uniform, either and decomposing it with degradation of quality by a manufacturing process, and the damage to the aquosity animal, etc. are reported. The fall of the physical properties by starch was not avoided and it was not satisfactory. For reduction of oxygen permeability, although the correspondence in vacuum evaporation of aluminum and silicon, etc. is also possible, it becomes a high cost.

[0006]As mentioned above, since there were many insufficient portions while the existing plastic had the feature, respectively, development of the plastic which the balance of intensity, collapsibility, moisture permeability, oxygen permeability, and cost was able to take was desired.

[0007]

[Problem(s) to be Solved by the Invention]The purpose of this invention is to provide the resin composition and its mold goods which solve a technical problem in conventional technology which was described above, have practically sufficient heat-resistant temperature, and have a moldability, solvent resistance, hypoxia transmissivity, low moisture permeability, transparency, moderate collapsibility, and a high mechanical strength.

[0008]

[Means for Solving the Problem]Polyolefine with heat resistance and a mechanical strength high [this invention persons] as a result of inquiring wholeheartedly that said technical problem should be solved, and a low moisture permeation coefficient, When pliability, hydrolysis resistance, and biodegradability mix a polymer with aliphatic ester structures whose oxygen permeability it is high and is low, It found out that a resin composition which will collapse by the time it does not stop a prototype by a microorganism which has sufficient mechanical strength for practical use, and in which a moldability, heat resistance, solvent resistance, and a low moisture permeation coefficient and oxygen permeability are shown was obtained. Especially, while aliphatic polyester carbonate has high compatibility with polyolefine and reveals sufficient raw collapsibility by reducing a degree of crystallinity of polyolefine in an obtained resin composition, It excelled in a mechanical physical property, found out that a resin composition with low moisture permeation coefficient and oxygen permeability was obtained, and resulted in this invention.

[0009]That is, this invention relates to a resin composition which consists of a polymer with aliphatic ester structures, and polyolefine, and its mold goods. Polymers in which a resin composition which consists of a polymer with aliphatic ester structures and polyolefine in more detail has aliphatic ester structures are aliphatic polyester carbonate and/or aliphatic polyester. Content of polyolefine of content of a polymer with aliphatic ester structures in a resin composition is 95 to 5 % of the weight five to 95% of the weight. Tensile strength is 20 or more MPa, and a moisture permeation coefficient of oxygen permeability is [heat deflection temperature / a tensile elongation rate / below 20

gmm/m² and day and Hayes of below 200 cc-mm/m² and day] 50 or less not less than 50% 60 degrees or more.

[0010]

[Invention embodiment] As a polymer with aliphatic ester structures in this invention, Polly 3-hydroxybutyric acid ester (PHB), polycaprolactone (PCL), Aliphatic polyester, aliphatic polyester carbonate, etc., such as polylactic acid (PLLA) which used as the main raw material polybutylene succinate (PBS) or a polybutylene succinate horse mackerel peat which uses succinic acid and butanediol as the main ingredients, and L lactic acid, are illustrated. Especially, especially aliphatic polyester carbonate is preferred.

[0011]With aliphatic polyester carbonate in this invention. A with a number average molecular weight of 10,000 or less produced by making aliphatic series dibasic acid and/or its derivative, an aliphatic dihydroxy compound, and/or a hydroxycarboxylic acid compound react aliphatic polyester oligomer, Carbonate unit content produced by making a carbonate compound react is more than 5 mol % at least, and weight average molecular weight by at least 100,000. Temperature of 190 ** and melt viscosity in 60 kg of load are characterized by the melting point being 70-180 ** at 2,000-50,000 poise.

[0012]A manufacturing method of aliphatic polyester carbonate by this invention, The 1st process of obtaining an aliphatic polyester oligomer from aliphatic series dibasic acid, its derivative and aliphatic dihydroxy compound, and/or a hydroxycarboxylic acid compound, And it comprises the 2nd process of making a carbonate compound reacting to an aliphatic polyester oligomer, and obtaining aliphatic polyester carbonate.

[0013]The 1st process is 100-250 ** in temperature under existence of a catalyst, and is a process of manufacturing a with a number average molecular weight of 10,000 or less polyester oligomer, removing water and a superfluous dihydroxy compound which carry out a byproduction with a reaction. It is preferred to consider it as decompression of 300 or less mmHg in order to promote a reaction.

[0014]The 2nd process is a process which a polyester oligomer and a carbonate compound which were obtained at the 1st process are made to react, and is used as the amount object of polymers, under existence of a catalyst, it is usually carried out at 150-250 **, and a hydroxy compound which sub** with a reaction is removed. Depending on the boiling point of a carbonate compound, it is considered as application of pressure in early stages of a reaction. It is preferred to adjust a decompression degree and to consider it as decompression of 3 or less mmHg eventually.

[0015]Carbonate unit content in aliphatic polyester carbonate can be made into a desired rate by controlling the amount of terminal hydroxyl groups of an aliphatic polyester oligomer. If there is too much carbonate unit content, the melting point of aliphatic polyester carbonate obtained will become low, and polymer which has practical heat resistance will not be obtained. On the other hand, if carbonate unit content increases, resolvability by a microorganism will become high. Therefore, as for carbonate unit content, it is preferred to consider it as quantity which has moderate biodegradability and can realize practical heat resistance, In this invention, it is preferred more than 5 mol % and to usually make carbonate unit content in aliphatic polyester carbonate into 5-30-mol % at least.

[0016]As aliphatic series dibasic acid used for manufacture of aliphatic polyester carbonate of this invention, A trowel which succinic acid is used as an essential ingredient, and is alike other than this, for example, uses together suitably oxalic acid,

malonic acid, glutaric acid, adipic acid, suberic acid, sebacic acid, dodecanoic acid, azelaic acid, etc. can be done. The above-mentioned aliphatic series dibasic acid may be those ester or an acid anhydride.

[0017]An aliphatic dihydroxy compound used for manufacture of aliphatic polyester carbonate of this invention, 1,4-butanediol is used as an essential ingredient, other than this, is alike, and for example, Ethylene glycol, a trimethylene glycol, propylene glycol, 1,3-butanediol, pentanediol, hexandiol, octanediol, neopentyl glycol, cyclohexanediol, cyclohexane dimethanol, etc. can be suitably used together.

[0018]As a hydroxycarboxylic acid compound used by this invention, lactic acid, glycolic acid, beta-hydroxybutyric acid, hydroxy pivalate, a hydroxyvaleric acid, etc. are illustrated, and these can also use derivatives, such as ester and cyclic ester.

[0019]these aliphatic series dibasic acid, an aliphatic dihydroxy compound, and a hydroxycarboxylic acid compound are independent, respectively -- it is, although it can use as a mixture and desired combination is possible, A thing of the melting point with the high degree of bundle which has moderate biodegradability and can realize practical heat resistance in this invention is preferred. therefore -- in this invention -- as an aliphatic dihydroxy compound -- as 1,4-butanediol and aliphatic series dibasic acid -- succinic acid -- respectively -- more than 50 mol % -- to contain is required.

[0020]As a concrete example of a carbonate compound used for manufacture of aliphatic polyester carbonate of this invention, Diphenyl carbonate, ditolyl carbonate, bis(chlorophenyl)carbonate, Diaryl carbonate, such as m-cresyl carbonate, again, Although aliphatic series carbonate compounds, such as dimethyl carbonate, diethyl carbonate, diisopropyl carbonate, dibutyl carbonate, JIAMIRU carbonate, and dioctyl carbonate, can be mentioned, it is not limited to these. An unsymmetrical carbonate compound and a cyclic carbonate compound which consist of a hydroxy compound of a different kind can also be used besides a carbonate compound which consists of the above-mentioned hydroxy compound of the same kind.

[0021]In this invention, the one-sort independence and two or more sorts of mixtures which are chosen from polyethylene, polypropylene, polyvinyl chloride, polyvinyl alcohol and polystyrene which are marketed generally [polyolefine], PMMA, and ABS plastics, or two or more sorts of copolymers are used.

[0022]A resin composition of this invention consists of a polymer and polyolefine which mainly have the above-mentioned aliphatic ester structures, A modifier, a bulking agent, lubricant, an ultraviolet ray absorbent, an antioxidant, stabilizer, paints, Conversion of a transesterification catalyst, various monomers, a coupling agent, an end processing agent, other resin, wood flour, starch, etc. other than various additive agents, such as colorant, various fillers, antistat, a release agent, a plasticizer, perfume, and an antimicrobial agent, can be added and carried out.

[0023]. It can obtain by mixing mechanically when manufacturing above temperature which at least one resin fuses. A method of manufacturing by mixing and pressurizing what ground both resin mechanically, After dissolving both resin in a solvent, it is also possible to manufacture by carrying out the cast of what obtained by mixing with a poor solvent and precipitate-izing, or dissolved both resin in a solvent, and removing a solvent, but it is not limited to them. Although not limited especially concerning a mixed device, a method of mixing using an extrusion machine is industrially recommended at a point which can be processed continuously in a short time.

[0024] or [that temperature at the time of mixing has high melt viscosity of resin below 100 degrees] -- or in order not to fuse, the range of 100 to 300 degrees is specifically preferred. Above 300 degrees, since a pyrolysis of resin happens, it is not desirable. Even if it is 300 degrees or less, in order to prevent coloring under an elevated temperature, degradation, a pyrolysis, etc., it is preferred to mix under a nitrogen atmosphere for a short time. Less than 20 minutes is recommended as concrete mixing time. A vent-port can be installed for removal of oligomer in resin, a residual monomer, generating gas, etc., and it can also mix under decompression.

[0025] A resin composition of this invention is not limited only to a simple blend of a polymer and polyolefine with aliphatic ester structures, and a copolymer etc. which are generated by an ester exchange reaction in a molten state, etc. under existence of a catalyst are contained.

[0026] 95 to 5 % of the weight is desirable still more preferred, and, as for content of a polymer with aliphatic ester structures in a constituent, 80 to 20 % of the weight is preferred. 5 to 95 % of the weight is desirable still more preferred, and, as for content of polyolefine, 20 to 80 % of the weight is preferred. Collapsibility by microorganism with content of a polymer with aliphatic ester structures sufficient at 5% or less cannot be given. Content of polyolefine cannot improve moisture permeability at 5% or less. As for a molecular weight of a polymer with aliphatic ester structures used here, 100,000 or more are desirable at weight average molecular weight by GPC of styrene conversion. Desired intensity is not attained or less by 100,000.

[0027] When they are able for collapsibility by a microorganism and pliability to become high and to make oxygen permeability low, when a rate of a polymer with aliphatic ester structures is high and a rate of polyolefine is high, transparency and moisture permeability are improved. A resin design according to a use and the purpose is possible.

[0028] Mold goods of this invention are articles fabricated using a resin composition of this invention, and as a concrete shaping gestalt and a forming process, An injection-molded product, extrusion, an inflation molding method, vacuum pressure sky mold goods, Although a blow molded article, textiles, multifilament, a monofilament, a rope, a net, textiles, knitting, a nonwoven fabric, a film, a sheet, a lamination, a container, foam, and various parts and other mold goods are illustrated, it is not limited to them.

Especially a resin composition of this invention has a good film moldability, for a multifilm use for agriculture, catabolic rate is eased and a film design of the suitable rate of decay according to a use, the area, and climate is attained.

[0029] Although it is preferred to mixed-pellet-ize a polymer which has aliphatic ester structures before shaping from the homogeneity of resin, intensity, appearance nature, etc., and polyolefine, it is in a state of a pellet about a polymer and polyolefine with aliphatic ester structures, Depending on the case, various additive agents can also be mixed simultaneously, it can supply to a molding machine directly, and mold goods can also be obtained. It is also possible by dissolving both resin in a solvent, casting or applying by solution states, and removing a solvent to obtain a film, a sheet, and other mold goods.

[0030] A resin composition and mold goods which are obtained have a high mechanical strength and practically sufficient softening temperature, and by the time they do not stop a prototype by a microorganism in the ground, activated sludge, and compost, they will collapse.

[0031]A resin composition of this invention and the biodegradability of mold goods can be adjusted with a molecular weight, loadings of a polymer with aliphatic ester structures, and polyolefine, and thickness of mold goods.

[0032]According to this invention, like the above, a resin composition and mold goods which have practically sufficient heat resistance and intensity, and collapsibility by a microorganism, low moisture permeability and hypoxia transmissivity can be obtained.

[0033]Next, an example explains this invention still in detail.

[0034]In this example, the melting point was measured using DSC (SSC 5000 made from SEIKO Electron). A molecular weight was measured as Mw of styrene conversion, and Mn by GPC (Showa Denko K.K. make GPC System-11 use) by using chloroform as a solvent. Carbonate unit content used NMR (NMR EX-270 by JEOL Co., Ltd.), and measured it by carbon magnetic resonance as a rate (mol %) of a carbonate unit over the sum total of a dicarboxylic acid ester unit and a carbonate unit.

[0035]Melt viscosity was measured by temperature of 190 **, and 60 kg of load using a flow tester (Shimadzu CFT-500C). A hydroxyl value of oligomer of aliphatic polyester carbonate and acid value were measured according to JIS K-1557. Heat deflection temperature applied to ASTM-D648 correspondingly, tensile physical properties applied to JIS-K7113 correspondingly, and it measured. Hayes was measured with a 50-micron film. Oxygen permeability measured a moisture permeation coefficient according to JIS-Z208 using the MOCON method.

[0036]An example agitator of manufacture of aliphatic polyester carbonate, a fractional distillation capacitor, A thermometer and a gas introducing pipe to the attached 50-l. reaction vessel The succinic acid 18,740g (158.7 mol), 21,430 g (237.8 mol) of 1,4-butanediol, 745 mg of zirconium acetylacetone, and the zinc acetate 1.40g were prepared, it reacted at temperature of 150-220 ** under a nitrogen atmosphere for 2 hours, and water was made to distill. Continued, ripe with the decompression degree 150 - a decompression degree of 80mmHg for 3 hours, and advanced dehydration, and also increased a decompression degree gradually, water and 1 and 4-butanediol were made to distill further so that it may become 2 or less mmHg of decompression degrees eventually, and a reaction was suspended in a place where the total amount of distillates became 10,460 g. A number average molecular weight of obtained oligomer was 1,780, terminal-hydroxyl-groups value was 102 KOHmg/g, and acid value was 0.51 KOHmg/g.

[0037]Next, 24,000 g of obtained oligomer was taught to the 50-l. reaction vessel which attached an agitator, a fractional distillation capacitor, a thermometer, and a gas introducing pipe, and 4,680 g of diphenyl carbonate was added. It was eventually considered as decompression of 1mmHg at temperature of 210-220 **, and a reaction was performed for 5 hours. The melting point is 104 **, weight average molecular weight (Mw) by measurement of GPC is 188,000, and the acquired amount object of polymers had 14.3% of carbonate unit as a polycarbonate ingredient by carbon-magnetic-resonance measurement. Melt viscosity was 10000poise, it dissolved in chloroform thoroughly and the amount of gel was not.

[0038]An aliphatic polyester carbonate pellet obtained in an example of example 1 manufacture is dried at temperature of 90 ** with a vacuum dryer for 10 hours, mixing with a V type blender so that polyethylene and a weight ratio may make 50/50, and supplying a biaxial extrusion machine (screw diameter 25mmphi, ratio-of-length-to-diameter=30) -- continuous -- strand-izing -- it pelletized and a resin mixture was

obtained. After drying a pellet of this resin mixture at temperature of 90 degrees for 5 hours or more, an injection molding machine (1000 t of clamping pressure) was supplied, and a specimen for a physical-properties examination was fabricated. As for tensile elongation, tensile strength of heat deflection temperature was [evaluation result of an obtained specimen] 40MPa 430% 85 degrees. A 50-micron film was created for this pellet by the T-die method, and physical-properties measurement was performed. Hayes was 20, oxygen permeability was 20 cc-mm/m² and day-atm, and moisture permeation coefficients were 12 g-mm/m² and day. 30% of decomposition was advancing by collapsibility examination in the ground of the film in 60 days. A physical-properties evaluation result is shown in table-1.

[0039]By the completely same operation as two to example 7 Example 1, a result of having changed a kind and the mixture ratio with aliphatic ester structures of a polymer (A) and polyolefine (B), and having performed physical-properties evaluation is made into Examples 2-7, respectively, and a result is shown in table-1.

[0040]A result is shown in table-1 by making into the comparative example 3 what performed what performed what performed the completely same shaping as one to comparative example 3 Example 1, and physical-properties measurement at aliphatic polyester carbonate 100% at comparative example 1 and polyethylene 100% at comparative example 2 and polypropylene 100%.

[0041]

[Effect of the Invention]The resin composition which consists of a polymer with the aliphatic ester structures concerning this invention, and polyolefine, Excel in a moldability and An injection-molded product, extrusion, vacuum pressure sky mold goods, a blow molded article, Textiles, multifilament, a monofilament, a rope, a net, textiles, It is suitable to obtain knitting, a nonwoven fabric, a film, a sheet, a lamination, a container, foam, and various parts and other mold goods, and the mold goods obtained have oxygen permeability sufficient mechanical strength, heat-resistant, and low and moisture permeability, and. It will collapse, by the time it does not stop the original form by a microorganism easily in the ground, activated sludge, and compost. For this reason, wrapping, agriculture, a fishing, a food field, and other recycling can use for a difficult use widely. For example, in the wrapping field, various packages are possible as a film and heat sealing is also possible. It can use for the coating material etc. of a multilayer film, the bowl for garden trees and string which cover earth surface with an agricultural field and keep soil warm, or manure, or can use for a fishing line and a fishing net as hygienic goods, such as medical-application material of a medical field, and sanitary items, further in the fishery field.

[0042]

[Table 1]

	脂肪族ポリ カルを持つ 重合体(A)	ポリオレイン (B)	混合割合 (A)/(B)	熱変形温度 (°C)	引張強度 (MPa)	引張伸度 (%)	ヘイズ (%)	酸素透過率 (cc·mm/m ² · day·atm)	透湿係数 (g·mm/E2 ·day)	生分解性 (重量減 少率 %)	燃焼熱 (cal/g)
実施例 1	P E C	PE	80/20	85	40	430	20	20	12	30	6,600
2	"	"	50/50	83	36	550	16	90	7	70	8,250
3	"	"	20/80	82	28	650	9	140	3	80	9,900
4	"	PP	50/50	103	44	560	14	25	6	60	8,250
5	"	P s t	"	95	42	210	10	160	11	55	7,550
6	PLA	PE	"	70	42	190	8	110	6	30	7,780
7	P B S A	"	"	79	35	620	17	100	7	65	8,250
比較例 1	P E C	-	100/0	87	46	360	24	16	18	>90	5,500
2	-	PE	0/100	80	17	700	5	300	0.5	0	11,000
3	-	PP	0/100	117	41	800	7	70	0.4	0	11,000